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Preparation, characterization and photodegradation of methylene blue based on TiO_2 microparticles modified with thiophene substituents

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The new microparticles, 2-formylthiophene (FT)/TiO_2 and (E)-1,2-bis(5-formyl-2-thienyl) ethylene (EBFTE)/TiO_2 were synthesized with a silane coupling agent. The prepared TiO_2 composites were characterized using Ultraviolet-Vis absorption (UV-Vis), X-ray diffraction (XRD), scanning electron microscope (SEM) and thermogravimetric analyzer (TGA). Methylene blue was used as a model material to examine the photocatalytic activities of the prepared catalysts under both Ultraviolet-Vis (UV) and visible (Vis) light. The enhanced photocatalytic activities were observed in the presence of (FT)/TiO_2 and EBFTE/TiO_2 under Vis light. It suggests that FT or EBFTE plays a block or active role in the photodegradation mechanisms under UV and Vis light irradiation, respectively.

TiO_2, methylene blue, microparticles, photocatalytic degradation, thiophene

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Organic dyes are widely used in textile industry and the released industrial waste has caused serious damages to the water system [1–5]. In 1976, Carey et al. [6] first reported that TiO_2 was used as a photocatalyst in the degradation of biphenyl and chlorobiphenyls. Frank and Bard [7] studied the photocatalysis oxidation of cyanide ion with oxygen in the presence of TiO_2 powders as a heterogeneous photocatalyst. TiO_2 with the non-toxicity, chemically stability and low cost is a dramatic photocatalyst in degradation of colored water. However, TiO_2 can only make use of ultraviolet (UV) light that accounted for about 3%–5% of sunlight due to its rather broad band-gap (3.2 eV) [1]. Therefore, researches have been done to explore the mechanism of photocatalytic degradation with TiO_2 [8–15] and improvement of the degradation efficiency.

Thus, some effective methods have been developed, such as dye-sensitization, ion doping and semiconductor coupling [16–18]. In particular, dye-sensitization is utilized to expand the spectral response region extending from UV light to visible (Vis) light. Sensitizers that showed a better energy match with the conduction band (CB) and the valence band (VB) of TiO_2 are introduced to improve the utilization efficiency of sunlight. The composites are desired to be active, Vis-responsive and highly stable [12]. For example, porphyrin/TiO_2 [19] and poly(acrylamide-co-(acrylic acid))/TiO_2 [20] were applied in photodegradation and showed high degradation efficiency. In addition, thiophene and its derivatives are considered as a kind of promising sensitizers due to its high absorption in Vis light region. Zhu et al. [21] and Lu and Yang [22] reported that polythiophene/TiO_2 and poly(3-hexylthiophene)/TiO_2 microparticles were synthesized and provided an apparent additive effect on their adsorption capacities under both UV light and Vis light.

However, small molecule organic compounds modified TiO_2 are seldom reported. On the other hand, (E)-1,2-bis-(2-thienyl) ethylene [23] was reported as a kind of high performance material in Vis light region with narrow energy

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gap and broad absorption. In this study, 2-formylthiophene (FT) and (E)-1,2-bis(5-formyl-2-thienyl)ethylene (EBFTE) modified TiO_2 composites were synthesized successfully with a silane coupling agent. The structure, morphology and thermal stability have also been investigated. In photodegradation experiment, the composites show high Vis light photocatalytic activity for the degradation of methylene blue (MB). Based on the data presented here, possible mechanisms are proposed in detail.

1 Experimental procedures

1.1 Materials

In this study, all chemical reagents and solvents were used without further purification except that DMF, $POCl_3$ and THF were redistilled. 3-aminopropyltriethoxysilane (APS, 99%) and thiophene (99%) were obtained from domestic chemical market. Other chemical reagents were of analytical grade. In addition, in the photodegradation experiment, the photocatalysts were well-prepared TiO_2, FT/TiO_2 and EBFTE/TiO_2 microparticles. MB was purchased from Chengdu Kelong Chemical Reagents Factory (Chengdu, China) and its solution was prepared with doubly distilled water. A 450 W high pressure mercury lamp (HPML) and a 40 W UV lamp were used as photodegradation light sources.

1.2 General characterization

The thermal behavior of the composites was performed with a TA SDTQ600 thermogravimetric analyzer (TGA, USA) under a dry nitrogen gas flow at a heating rate of 10°C/min. X-ray diffraction (XRD) was measured on an XD-3 powder diffractometer (Purkinje General Instrument Co., Beijing, China). Investigation of the morphology of the microparticles of these composites was carried out by using an S-4800 field-emission scanning electron microscope (SEM, Hitachi, Japan). Ultraviolet-Vis absorption (UV-Vis) was obtained on a UV-2550 spectrometer (Shimadzu, Japan). The suspension was centrifuged with a Xiang Yi TDZ4A-WS brachytely desk centrifuge (Changsha, China).

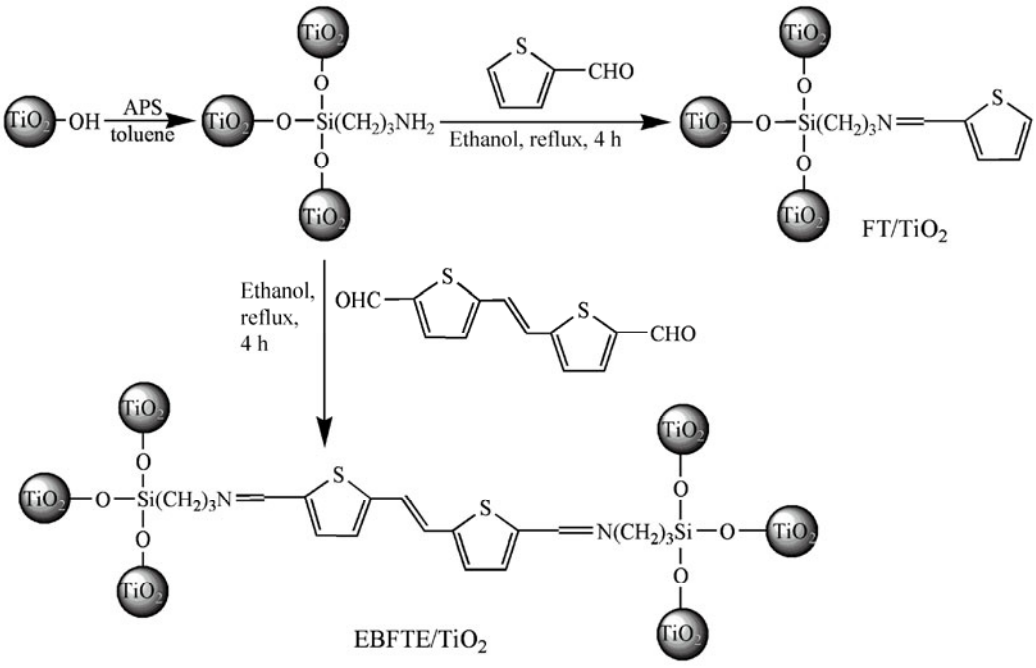
1.3 Sample preparation

(1) Preparation of TiO_2, FT and EBFTE. The main process of the synthesis section is shown in Scheme 1. TiO_2 microparticles, surface modified TiO_2 microparticles with APS were prepared according to the literature [20,22], respectively. In addition, 2-formylthiophene (FT) and (E)-1,2-bis(5-formyl-2-thienyl)ethylene (EBFTE) were synthesized by Vilsmer-Haack reaction as the reported literature [24].

(2) Preparation of FT/TiO_2 and EBFTE/TiO_2 composite microparticles. The 5 g modified TiO_2 microparticles and 100 mL ethanol were added to a 250 mL flask. The 1.6 g FT or 3.4 g EBFTE was mixed with 10 mL ethanol, then added dropwise into the flask under N_2, and refluxed for 4 h. After cooling down, the precipitate was filtered, washed with ethanol and dried in a vacuum oven at 60°C for 24 h to obtain FT/TiO_2 and EBFTE/TiO_2 microparticles.

1.4 Photocatalytic degradation

The photocatalytic activity of TiO_2, FT/TiO_2 and EBFTE/TiO_2 microparticles was evaluated by measuring the



Scheme 1 The synthesis route of modifying FT and EBFTE onto the TiO_2 surface.

photodegradation rate of MB solution under UV and Vis light irradiation. The initial concentration of MB was 0.1 mg/L, and 15 mg catalyst powders were added, and then stirred with a magnetic stirrer in the dark previously. The degradation rate of MB solution was monitored by the absorption peak at λ_{max} = 664 nm corresponding to methylene blue molecule with an UV-Vis spectrophotometer until MB was completely degraded.

2 Results and discussion

2.1 UV-Vis absorption spectra

The normalized absorption spectra of FT, EBFTE, TiO_2, FT/TiO_2 and EBFTE/TiO_2 are shown in Figure 1. The maximum absorption peak of TiO_2 is observed at about 276 nm. The absorption of FT/TiO_2 is significantly blue shifted to λ_{max} = 262 nm, owing to an introduction of broad band FT group. EBFTE exhibits an absorption peak at λ_{max} = 395 nm and a shoulder at about 410 nm. EBFTE/TiO_2 exhibits a widened absorption band centered at λ_{max} = 382 nm, extending the absorption to Vis light range, which was assigned to $\pi - \pi^*$ transition of the conjugated thiophene-vinyl system. It suggests that TiO_2 is effectively modified by EBFTE. Therefore, the EBFTE/TiO_2 composites could be excited to generate more photoelectrons and enhance the photocatalytic activity under Vis light irradiation.

2.2 XRD studies

The diffraction patterns for TiO_2, FT/TiO_2 and EBFTE/TiO_2 are shown in Figure 2. From Figure 2a, TiO_2 exhibits three strong diffraction peaks at 27°, 36° and 54°, respectively, which is assigned to the rutile phase of TiO_2 according to the standard spectrum (JCPDS No. 88-1175) [25]. Figure 2b shows similar peaks to TiO_2 particles which suggests that TiO_2 modified by FT has hardly any effect on its crystallization performance. From the XRD patterns of EBFTE/TiO_2 composite mircroparticles (Figure 2c), only a weak, broad diffraction peak for EBFTE/TiO_2 is detected, and others do not appear, which demonstrates that EBFTE/TiO_2 provides with an amorphous characteristics. It suggests that the morphologic structure of TiO_2 by the dye-modified method can be changed from the crystalline state to an amorphous state. Simultaneously, the weakened diffraction peaks can be explained by kinds of interactions between EBFTE chains and TiO_2 microparticles.

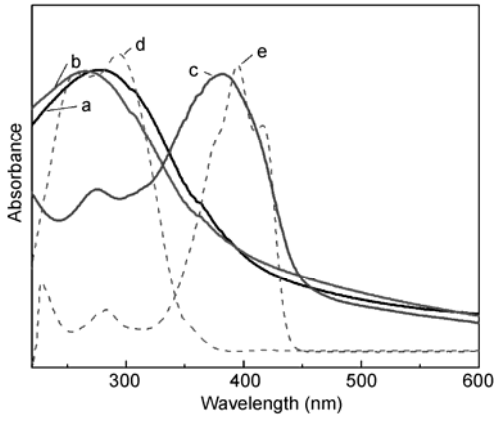


Figure 1 Normalized UV-Vis spectra of TiO_2 (a), FT/TiO_2 (b), EBFTE/TiO_2 (c), FT (d), EBFTE (e) in CH_2Cl_2 solution.

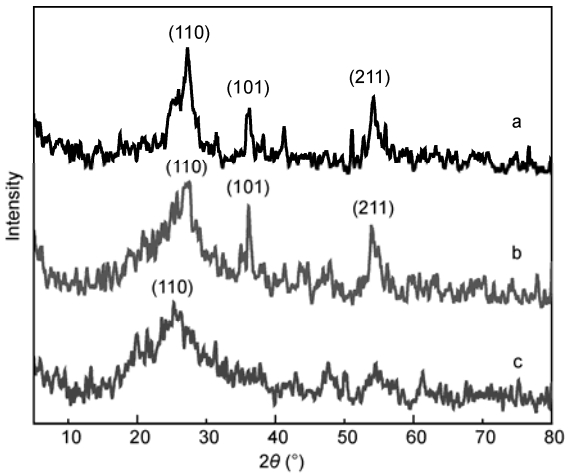


Figure 2 XRD patterns of TiO_2 (a), FT/TiO_2 (b) and EBFTE/TiO_2 (c).

2.3 SEM studies

To further investigate the morphology of TiO_2, FT/TiO_2 and EBFTE/TiO_2, their SEM images were measured. As shown in Figure 3(a), nonmodified TiO_2 exhibits some 0.5–1 μm-sized microspheres and their aggregation. Similarly, FT/TiO_2 still keeps the regular spherical morphology and smooth surface, but the main size is reduced to 0.3 μm approximately (Figure 3(b)). From Figure 3(c), the irregular particles or powders with a non-uniform grain size are observed, which further confirms the results of XRD measurement. In addition, nonmodified TiO_2 and FT/TiO_2 exhibit more or less aggregation. However, EBFTE/TiO_2 shows a better distribution which is a reason that sharp XRD peaks of TiO_2 in the composites gradually disappeared. Therefore, we conclude that EBFTE/TiO_2 with excellent distribution character may be beneficial to the high photocatalytic activity.

2.4 TGA studies

The TGA experiment was performed to investigate the thermal stability of FT/TiO_2 and EBFTE/TiO_2. The TGA curves of FT/TiO_2 and EBFTE/TiO_2 are shown in Figure 4. In the case of FT/TiO_2 and EBFTE/TiO_2, it is clear that there are two major stages of weight loss. The first major weight loss of 7% is noticed under the temperature of 100°C, which is assigned to the adsorbed water on microparticles surface. However, the residue mass for FT/TiO_2 and EBFTE/TiO_2 is about 82% (at 580°C) and 79% (at 593°C) at the

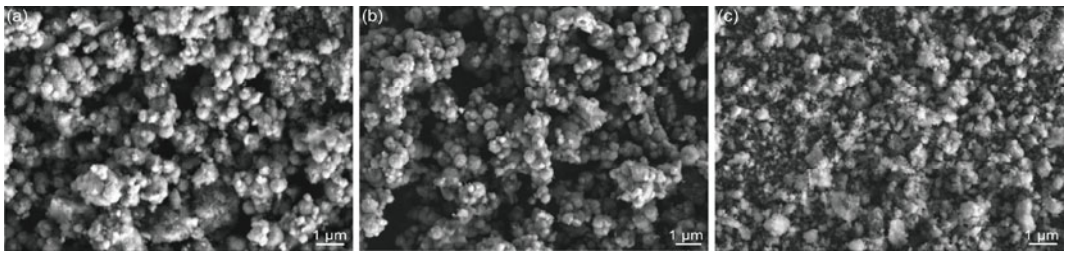


Figure 3 SEM images of (a) TiO_2, (b) FT/TiO_2 and (c) EBFTE/TiO_2.

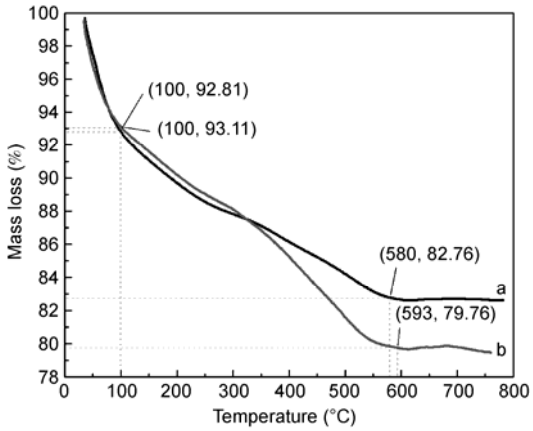


Figure 4 Thermal gravimetric analysis of FT/TiO_2 (a) and EBFTE/TiO_2 (b).

second stage, respectively. It is reported that TiO_2 had the good stability below 30600°C [26]. Consequently, the second weight loss may be attributed to the loss of APS-FT or APS-EBFTE, respectively. According to the above results, it is also clear that both TiO_2-APS-FT and TiO_2-APS-EBFTE are of the relative thermal stability.

2.5 Photocatalytic degradation properties

The intensity of absorption (at a wavelength of 664 nm) was recorded at different time intervals and converted to the concentration of MB solution. The typical time-dependent of $-\ln(C_t/C_0)$ under UV and Vis light irradiation are shown in Figure 5(a) and (b), respectively. It has been proved that the reaction rate constant k could be calculated using pesudo-first-order pattern, based on the equation [27]: $\ln(C_t/C_0) = -kt$ (where t is the irradiation time, C_0 is the initial concentration of the MB solution and C_t represents the concentration of MB solution at later times t). The reaction rate constants k are obtained by the slope of the straight lines (Figure 5(a) and (b)) and the comparison of k under UV and Vis light irradiation for different prepared-catalysts are shown in Figure 5(c). It is clearly shown that TiO_2 exhibits much higher photocatalytic activity than that of prepared FT/TiO_2 and EBFTE/TiO_2 under UV light irradiation, while EBFTE/TiO_2 displays a significant improvement of photocatalytic activity under Vis light irradiation in comparison with TiO_2 and FT/TiO_2.

Experimental studies have suggested that photocatalytic

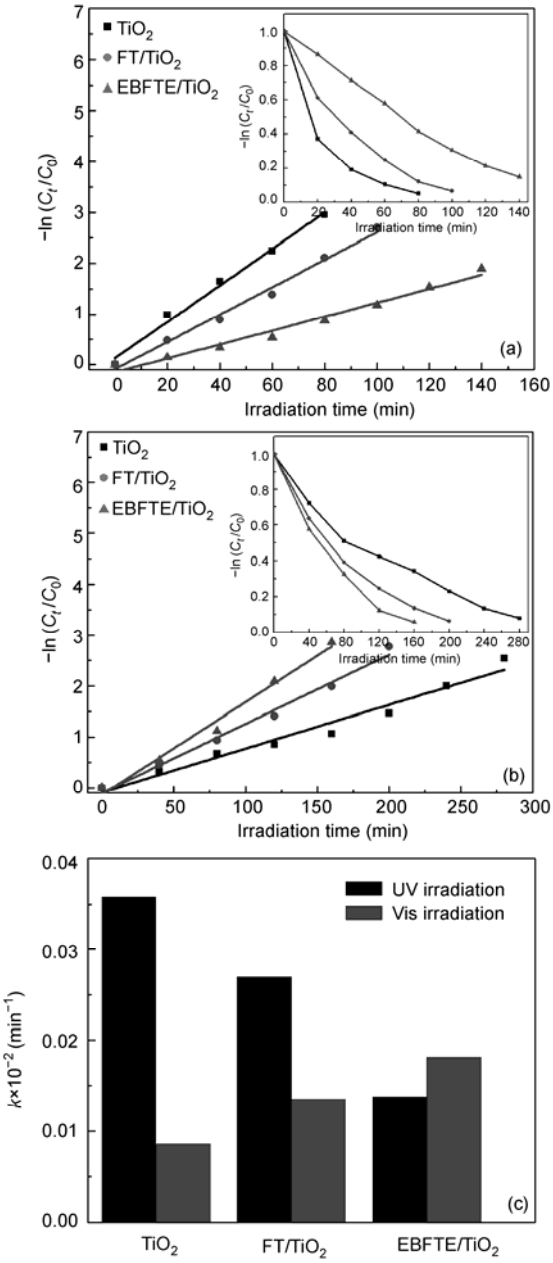


Figure 5 (a) $\ln(C_0/C_t)$ as a function of UV irradiation for TiO_2, FT/TiO_2 and EBFTE/TiO_2, inset: degradation rate of TiO_2, FT/TiO_2 and EBFTE/TiO_2 under UV irradiation; (b) $\ln(C_0/C_t)$ as a function of Vis irradiation for TiO_2, FT/TiO_2 and EBFTE/TiO_2, inset: degradation rate of TiO_2, FT/TiO_2 and EBFTE/TiO_2 under Vis light irradiation; (c) photocatalytic reaction rate constants (k) for TiO_2, FT/TiO_2 and EBFTE/TiO_2 under UV and Vis light irradiation.

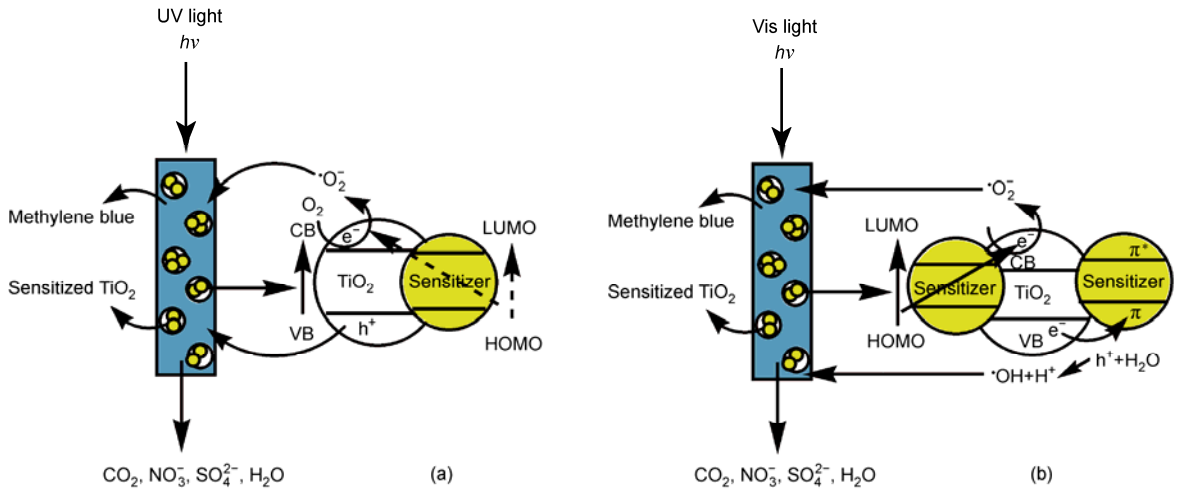


Figure 6 Mechanism of photocatalytic degradation (a) under UV light and (b) Vis light, respectively.

degradation of MB under UV light irradiation is mainly attributed to TiO_2 action in the UV region, and that FT and EBFTE display more or less contrary action in the degradation process of MB solution. As is shown in Figure 6(a), with UV light irradiation ($h\nu \geqslant$EG = 3.2 eV), the transition of electrons from the CB to the VB generates electron-hole pairs which migrate to the surface of TiO_2, FT/TiO_2 and EBFTE/TiO_2. Subsequently, the charge separation drives redox reactions with absorbed MB and further decomposes to an almost complete degradation, competing with their disappearance due to mutual recombination [26,28]. However, it is possible that the decreased photocatalytic reaction rate is attributed to the coverage of TiO_2 surface by FT and EBFTE which play the block role under UV light irradiation.

As shown in Figure 1, nonmodified TiO_2 can only absorb UV light to generate electron-hole pairs but cannot be excited by Vis light, while EBFTE/TiO_2 exhibits a strong absorption in the Vis light range. Herein, the enhancement of photocatalytic activity of EBFTE/TiO_2 under Vis light irradiation may be explained in Figure 6(b). When excited by Vis light, EBFTE promoted the charge separation to generate the photoelectrons. The photoelectrons are readily injected to the CB of TiO_2, and oxygen adsorpted on the surface of TiO_2 captures the injected photoelectrons to generate a series of powerful oxidative free radicals. At the meantime, a positive charged hole (h^+) might be formed by electron migrating from the VB of TiO_2 to the π-orbital, which can react with H_2O to generate ·OH [29] and these free radicals decompose MB completely, thus leading to the higher photocatalytic activity than that of nonmodified TiO_2. On the other hand, it should be pointed out that MB as a sensor may decompose itself. By exposing to light, it generates electrons and transfers electrons that react with dissolved oxygen to form hydroxyl radical under Vis irradiation [30,31]. That is why MB can be degraded by nonmodified TiO_2 and FT/TiO_2 although TiO_2 and FT/TiO_2 has no absorption in Vis light region. In addition, the smaller size of FT/TiO_2 and better distribution of EBFTE/TiO_2 (Figure 3) also play a active role in degradation of MB.

3 Conclusions

A photocatalytically degradable FT/TiO_2 and EBFTE/TiO_2 were synthesized successfully with APS and displayed a relative stability identified by UV-Vis spectra and TGA, respectively. XRD and SEM implied there are some interactions between FT or EBFTE and TiO_2 microparticles. Besides, FT/TiO_2 and EBFTE/TiO_2 microparticles were relatively better in dispersion than nonmodified TiO_2. In addition, the results of photodegradation experiments indicate that FT/TiO_2 and EBFTE/TiO_2 play a block role in degradation process under UV irradiation while present a significantly enhancement of photocatalytic activity compared with nonmodified TiO_2 under Vis light irradiation. Concerning the possible mechanism, a key channel leading to higher photodegradation efficiency seems to enhance the conjugate degree of sensitizers modified on the surface of TiO_2.

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